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(54) SULPHUR-BURNING PROCESS

(71) We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, a body corporate organised under the Laws of Germany, of 14 Reuterweg, Frankfurt-on-the-Main, Germany, do hereby declare the invention for which we

prayer that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing sulphur dioxide by a stagewise combustion of elemental sulphur with the aid of oxygen-containing gases. Numerous processes for producing sulphur dioxide have been proposed, most of these processes involving roasting of sulphur-containing ores, particularly pyrites, or combustion of elemental sulphur. These processes may be carried out in roasting furnaces which include multiple hearth furnaces, fluidized bed furnaces and rotary kilns. Furnaces for burning elemental sulphur include mainly fluidized bed furnaces and preferably atomizing burners of various types.

Roasting and combustion processes are controlled so that the sulphur is roasted or burnt as completely as possible to form gases which contain sulphur dioxide. In order to accomplish that object, it has been proposed to provide in a sulphur-burning furnace, which is supplied with compressed air, a superheater in the form of a horizontal plate, which forces the gas to flow along a predetermined path and prevents the escape of sulphur dust or fumes, or to introduce sulphur powder into a stream of air or oxygen in such a manner that the sulphur is ignited at the time at which it meets the stream of air or oxygen and is burnt immediately or to maintain the flow of the reactants in certain paths and directions. It has also been proposed to introduce elemental sulphur into a highly compressed charge of air and to promote

burning of the sulphur over an extended period according to the Diesel or like constant pressure principle, the sulphur being burnt, for example, as fuel in a Diesel engine.

Numerous proposals have been made for structural details of sulphur-burning furnaces. Additional processes are directed to the processing of elemental sulphur to produce a sulphur dioxide-containing gas which is as pure as possible, i.e., which is free from sulphur trioxide. This object may be accomplished by burning the sulphur in the presence of a surplus of sulphur fumes and, if desired, under superatmospheric pressure, in order to reduce the temperature at which the combustion takes place, or by passing minute bubbles of heated oxygen or air through hot liquid sulphur. In another process, the combustion gas should be free of residual elemental sulphur, which is often left in the combustion of sulphur. To that end, the combustion air is divided into one primary stream and two secondary streams.

In order to recover the heat content of the combustion gases formed by the combustion of sulphur and to produce a gas which can be catalyzed to form sulphur trioxide, it has been proposed to burn the sulphur with the aid of a first stream of pre-dried air, to cool the resulting gas stream in a heat exchanger, to dilute the cooled gas stream with a second stream of pre-dried air and to supply the diluted stream to a catalytic reaction plant.

The earlier proposed processes have the disadvantage that only a small throughput is possible in the combustion of sulphur. Whereas this disadvantage is avoided in the more recently proposed processes and apparatus, these suffer from another disadvantage. An increase in throughput results as a rule in a higher concentration of sulphur dioxide in the combustion gas, par-

ticularly when the combustion is supported by oxygen-enriched air or oxygen, and results also in a higher combustion temperature. Higher combustion temperatures promote the formation of oxides of nitrogen so that these processes result in a gas which contains sulphur dioxide and which may contain considerable amounts of oxides of nitrogen. Such oxides of nitrogen may result in contamination of the end product, whether this consists of liquid sulphur dioxide or sulphuric acid, and also give rise to considerable corrosion problems.

According to the present invention there is provided a process for producing sulphur dioxide, wherein elemental sulphur is burnt first at substantially atmospheric pressure in the presence of free oxygen-containing gases in a quantity which is less than that which is required stoichiometrically to produce sulphur dioxide, and wherein the resulting gases which contain sulphur dioxide and sulphur are cooled by passing them through a heat exchanger and are then after-burnt with the aid of free oxygen-containing gases.

With the present process it is possible to obtain a high throughput and the production of a pure combustion gas which contains sulphur dioxide.

Preferably the whole quantity of free oxygen-containing gases required for the combustion of the sulphur is divided in such a manner that 70 to 95% is used in the combustion stage and 30 to 5% in the after-burning stage.

In order to ensure that the resulting gases will contain virtually no oxides of nitrogen, the after-burning is preferably carried out at a temperature below 1000°C.

An advantage of the present process is that, because the amount of sulphur which is reacted by after-burning is relatively small compared with the amount of sulphur which is reacted in the entire process and the heat of reaction produced by after-burning is small, the after-burning will not result in a substantial change in temperature, e.g. by not more than 20-40°C. As a result, the gases which leave the heat exchanger may be at a higher temperature than is otherwise permissible, e.g., for the gases received by the catalytic reaction plant, and a smaller heat exchange surface area is sufficient in the heat exchanger.

Depending upon the concentration of sulphur dioxide which is desired, e.g., in the catalytic reaction plant, the temperature of the gas which leaves the heat exchanger may be adjusted so that the admixing of free oxygen-containing gases for the after-burning results in a gas mixture at a temperature which is an optimum for the catalytic reaction plant.

The rate at which the sulphur dioxide-

containing gas is required may be subjected to fluctuations, which in previously proposed processes must be compensated by changes in the heat exchange surface areas of the heat exchangers. In the present process, the division of the free oxygen-containing gases can be changed in a simple manner in the case of such fluctuations so that the heat exchange surface area remains constant and the temperature of the gas leaving the heat exchanger may be adjusted within small limits, e.g., 20-40°C., to the required value by the selection of a proper quantity of heat generated by after-burning.

Where gases are desired which have a sulphur dioxide concentration which is much below the concentration which can be obtained by the present process, e.g., gases having a sulphur dioxide concentration in the range of 8-12% by volume, such as are commonly used in a catalytic reaction process for producing sulphuric acid, it is desirable to add further free oxygen-containing gases in a gas mixer outside the after-burning zone.

The temperature may also be adjusted by preheating the free oxygen-containing gases for the after-burning stage and/or the diluting stage.

The present process is carried out in such a manner that the combustion gases leaving the heat exchanger have a certain content of elemental sulphur. This sulphur content can be desirably adjusted by performing the combustion of sulphur in a main combustion stage and in a secondary adjusting stage, which permits of a fine adjustment.

The technologically desired sulphur content in the combustion gas which leaves the combustion stage will depend upon the temperature on the heat exchange surfaces in the heat exchanger or *vice versa* because the temperature of the heat exchange surfaces must not be lower than the dew point of the sulphur in the combustion gas.

The sulphur may be burnt in conventional sulphur-burning furnaces, preferably in atomizing burners, such as are described in the Specification of German Patent No. 1,178,407, where combustion is effected at atmospheric pressure.

Depending upon the degree of combustion, the gases which leave the sulphur-burning furnace have a temperature of 1,300 to 1,600°C. and contain 10 to 200 grams sulphur per standard cubic metre. The oxygen content of the combustion gases is virtually zero.

The heat exchangers are conventional heat exchangers, and may be waste heat boilers for the generation of steam.

The gases which leave the heat exchanger may be after-burnt in a chamber which is lined with a refractory material or pro-

vided with cooling tubes and which either consists of a separate unit of construction succeeding the heat exchanger or is disposed in the gas outlet of the heat exchanger and structurally combined with the latter.

In order to enable the invention to be more readily understood, reference will now be made to the accompanying drawing which illustrates diagrammatically and by way of example an embodiment thereof and which is a plant diagram of a preliminary stage in the production of sulphuric acid.

Referring now to the drawing, elemental sulphur is supplied in liquid form through a conduit 1 to a combustion furnace 2, to which oxygen-containing gas, such as air, oxygen-enriched air, or oxygen, is supplied through a conduit 3. The resulting combustion gases which contain hot elemental sulphur flow through a conduit 4 into a heat exchanger 5, where they are cooled. In a unit 6, the gases, which still contain elemental sulphur are after-burnt with the aid of oxygen-containing gases supplied through a conduit 7. Additional oxygen-containing gases supplied through a conduit 9 are mixed with the combustion gases in a mixer 8 to provide the desired concentration of sulphur dioxide. The sulphur dioxide-containing gas finally flows through a conduit 10 to a catalytic reaction vessel 11.

The process according to the invention will be explained more fully with reference to the following examples:

Example I

This Example illustrates the production of a gas which contains 10% by volume of sulphur dioxide and is to be processed to form sulphuric acid.

Elemental sulphur in liquid form and air were supplied through the conduit 1 to an atomizing burner provided in the combustion furnace 2 at rates per hour of 8,400 kilograms and 27,500 standard cubic metres, respectively. Combustion resulted in an oxygen-free gas which was at a temperature of about 1600°C. and contained 20.6% sulphur dioxide by volume and about 20 grams sulphur vapour per standard cubic metre. The oxygen-free gas was supplied through the conduit 4 into a waste heat boiler 5, in which it was cooled to about 750°C.. The unit 6 for after-burning the elemental sulphur was supplied through the conduit 7 with air at a rate of 4,400 standard cubic metres per hour. The mixer 8 was supplied through the conduit 9 with air at a rate of 25,600 standard cubic metres per hour. The gas which was supplied to the catalytic reaction vessel through the conduit 10 had a temperature of about 450°C. and a sulphur dioxide concentration of about 10% by volume. The output gas was discharged at a rate of 57,500 standard cubic

metres per hour and contained 16.8 metric tons of sulphur dioxide per hour.

Example 2

This Example illustrates the production of a gas which contains 18% by volume of sulphur dioxide and which is intended, e.g., for sulphurizing reactions in organic chemistry.

An atomizing burner provided in the combustion furnace 2 was supplied through the conduit 1 with elemental sulphur in liquid form and air at a rate per hour of 8350 kilograms and 25,700 standard cubic metres. The combustion resulted in a gas which was at a temperature of about 1600°C. and contained 20.6% sulphur dioxide and 20 grams sulphur vapour per standard cubic metre. The oxygen-free gas was supplied through the conduit 4 into a waste heat boiler 5, in which it was cooled to about 440°C.. The unit 6 for after-burning the elemental sulphur was supplied with air at a rate of 2,150 standard cubic metres per hour and the mixer 8 was supplied through the conduit 9 with air at a rate of 4,150 standard cubic metres per hour. The gas which was discharged through the conduit 10 for consumption had a temperature of 450°C. and a sulphur dioxide concentration of about 18% by volume. The output per hour amounted to 32,000 standard cubic metres of gas, which contained 16.7 metric tons of sulphur dioxide.

WHAT WE CLAIM IS:—

1. A process for producing sulphur dioxide, wherein elemental sulphur is burnt first at substantially atmospheric pressure in the presence of free oxygen-containing gases in a quantity which is less than that which is required stoichiometrically to produce sulphur dioxide, and wherein the resulting gases which contain sulphur dioxide and sulphur are cooled by passing them through a heat exchanger and are then after-burnt with the aid of free oxygen-containing gases.

2. A process as claimed in Claim 1, wherein the free oxygen-containing gases required for the complete conversion of the sulphur to sulphur dioxide are divided in such manner that 70 to 95% is used in the first stage and 30 to 5% is used in the after-burning stage.

3. A process as claimed in Claim 1 or 2, wherein the after-burning is carried out at a temperature below 1000°C..

4. A process as claimed in Claim 1, 2 or 3, wherein the temperature of the gases leaving the after-burning stage is adjusted to a desired value by the division of the free oxygen-containing gases which are required for the complete conversion of the sulphur to sulphur dioxide.

5. A process for producing sulphur dioxide substantially as hereinbefore described with reference to the accompanying drawing and/or in either of the foregoing Examples.
- 5 6. Sulphur dioxide produced by the process claimed in any preceding claim.

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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*